

THE EFFECT OF TORSION - VIBRATION COUPLINGS ON THE ν_9 AND ν_1 BANDS IN THE $\text{CH}_3\text{OO}\cdot$ RADICAL

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There are three CH stretch modes in the $\text{CH}_3\text{OO}\cdot$, namely the totally symmetric stretch, ν_2 , the out-of-phase symmetric stretch, ν_1 , and the antisymmetric stretch, ν_9 . However, only two strong partially rotationally resolved vibrational transitions are observed in the CH stretch region of the infrared spectrum of $\text{CH}_3\text{OO}\cdot$. Moreover, the Q-branches of both bands are significantly broader than the simulations using an asymmetric rigid rotor model. Previously, the rotational contour of the ν_2 band in the experimental spectrum has been simulated by considering the fundamental as well as sequence band transitions involving torsionally excited levels populated at room temperature^a. Using a four dimension Hamiltonian that involves the three CH stretches and the CH_3 torsion, the torsional sequence bands of the ν_2 stretch were calculated to be slightly shifted from the origin band as a result of the couplings between the CH stretches and CH_3 torsion which are particularly large due to an accidental degeneracy between the combination level involving the ν_2 stretch and n quanta in the CH_3 torsion and the combination level involving the ν_1 or ν_9 stretch and $n - 1$ quanta in the CH_3 torsion. In this study we focus on the part of $\text{CH}_3\text{OO}\cdot$ vibrational spectrum containing the ν_1 and ν_9 bands. Along with the 4-dimensional Hamiltonian which was used to simulate the spectra in the ν_2 region, we analyze the effect of torsion-stretch couplings on the ν_1 and ν_9 bands based on the model developed by Hougen^b to describe methanol. To account for the accidental degeneracies in CH_3OO , we extend the previous model to include the combination levels involving the ν_2 stretch and the CH_3 torsion. Unlike the torsional sequence bands and fundamental of ν_2 , the tunneling splittings of the torsional sequence bands and fundamentals of ν_1 and ν_9 have different signs, which results in the weak intensity of ν_1 fundamental and broadening in the rotational contour of the torsional sequence bands of ν_9 . The simulation of the ν_9 and ν_1 bands including the torsional sequence bands using the parameters which are consistent with the ones used in the simulation of the ν_2 band is in good agreement with the experimental spectrum.

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